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Transients in Thermal Isomerization of Cyclobutene by the Variable Encounter Method. Vibrational Energy Transfer and Relaxation at Lower Temperatures.

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An investigation of transients in cyclobutene vibrational relaxation by the VEM method has been made. Temperatures in the region 429 K to 778 K were used. Cyclobutene molecules isomerize to butadiene when transported above the critical threshold E_0. The collision efficiency of the wall increases with lowering of temperature, and strong collider behavior is obtained below 450 K. The data are described by a gaussian form of the collisional transition probability function. An exponential form of the probability function cannot fit all of the data.

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Transients in Thermal Isomerization of Cyclobutene by the Variable Encounter Method. Vibrational Energy Transfer and Relaxation at Lower Temperatures.*

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Abstract

Vibrational energy transfer and relaxation in the thermal isomerization of cyclobutene to 1,3-butadiene has been studied over the temperature range 429 K - 778 K using the Variable Encounter Method. Reactors characterized by various mean number of collisions, m , per encounter of a substrate molecule with the reactor (m = 2.6, 5.9, 8.5 and 27.2) were used. Strong collider behavior in collisions of substrate with a seasoned fused quartz wall was observed at lower temperatures (below 450 K) as evidenced by the coincidence of values of the probability of reaction per collision, $\bar{P}_c(m)$, obtained in VEM reactors having different m values. The average energy transferred to the wall per deactivating collision, $\langle\Delta E'\rangle$, increased strongly as temperature decreased, from $\langle\Delta E'\rangle = 2150\ cm^{-1}$ at 764 K to $> 6000\ cm^{-1}$ at 460 K. Various forms of models for the probability of energy transfer in down transitions were applied to data.

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Introduction

The Variable Encounter Method (VEM) has been shown to be a technique whereby studies can be made of energy transfer between a hot surface and gaseous molecules in the transient region. Investigations have been reported previously on cyclopropane-d_2 [1], cyclobutane [2], cyclopropane [3,4] and methylcyclopropane [5]. The efficiency for deactivating energized molecules has been found to decrease significantly with increase of temperature in the range 750 K - 1150 K.

The isomerization of cyclobutene to 1,3-butadiene has been studied in conventional thermal systems in the temperature range 400 K-450 K [6]. The high pressure first order rate constant was found to be given by the expression, $k(s^{-1}) = 2.5 \times 10^{13} \exp(-32900/1.987T)$. The reaction is unaffected by surface catalysis and, coupled with its low critical threshold energy, seemed ideal for the purpose of applying VEM at temperatures much lower than were feasible in the previous work. In this paper we present the results of our work with this molecule studied on a seasoned quartz surface over the temperature range 429 K - 778 K. A preliminary account has appeared [7].

Experimental

The reaction system, reactors and procedure were identical to those described previously [2]; these reactors were characterized by mean numbers of collisions per encounter, m , of 27.2, 8.5, and 2.6. In addition, an m = 5.9 reactor was also used. Reactor temperatures were controlled to ± 1°C. Temperature gradients for the 27.2 and 8.5 reactor varied between ± 6°C at the highest temperature to ± 2°C at the lowest temperature used. For the 2.6 reactor, temperature gradients at the highest temperature were ± 10°C and ± 4°C at the lowest temperature. In order to test the assumption that the temperature gradients near the tops of the reactors were negligible and to verify that the average temperatures used were correct, the stainless steel heater block was replaced with a stirred oil bath at 476 K ± 0.2°. The observed reaction rates were identical to those obtained using the heater block. In an experiment designed to simulate a much worse temperature gradient than any encountered, the oil bath level was lowered from its original level (2-3 mm above the top of the m = 2.6 reactor) to a level ∿ 1-2 mm below the top of the reactor. The decrease in the observed reaction rates was less than 20%. After trap-to-trap distillation, cyclobutene showed no impurity greater than 0.05% upon analysis by gas chromatography. Prior to kinetic runs, the cyclobutene reactant was thoroughly degassed. The reactors were aged by pyrolysis of cyclobutene at ∿ 4×10^{-4} torr for 24-48 hours at the highest temperature used for that reactor. Additional aging at even higher temperature, e.g., 1100 K for the m = 2.6 reactor, had no effect.

The reaction rate was measured by adding aliquots of cyclobutene from a gas burette to the reaction vessel, pyrolyzing the reactant for measured times and then rapidly freezing the reaction mixture in a glass wool packed trap cooled to 77 K. A measured freeze-down time correction of ∿ 10 s was added

to the measured pyrolysis time.

Analysis of the reaction mixture was accomplished by gas chromatography with use of a 6 ft 1/8" i.d. column of 28% squalane on 60-80 mesh fire brick and flame ionization detection.

Results and Calculations.

The isomerization of cyclobutane to 1,3-butadiene was investigated over the temperature range 429 K to 778 K at an initial pressure of $\sim 1.7 \times 10^{-4}$ torr cyclobutene. 1,3-butadiene was the only detectable product. A mass balance to better than 95% was observed.

At each temperature first-order rate plots were accurately linear and went through the origin. From these plots, which normally composed the result of at least 7 different run times, an apparent first order rate constant was determined. The standard deviation of the slope of these plots was typically 1%.

The rate constants were converted into the mean probability of reaction per collision with the reactor wall, $\bar{P}_c(m)$, in the manner described previously [1]. Values of $\bar{P}_c(m)$ are given in Table I for m = 2.6, 8.5 and 27.2. A plot of $\log_{10} \bar{P}_c(m)$ vs temperature is given in Fig 1 along with some more limited data obtained in the m = 5.9 reactor. A stochastic computer simulation procedure of the collisional processes has also been described previously [1]. Various models for the probability of a given down transition, p_{ij}, of an energized molecules of energy E_j going to energy E_i, were investigated:

Model FE ('flat' exponential): $p_{ij} = c_1 \exp(-\Delta E/\langle\Delta E\rangle)$;

Model FG ('flat' gaussian): $p_{ij} = c_2 \exp\{-(\Delta E-\Delta E_{mp})^2/2\sigma^2\}$;

Model LG ('linear' gaussian): $p_{ij}=c_3 \exp\{-(\Delta E-\Delta E_{mp})^2/2\sigma^2\}$, where $\Delta E_{mp}(cm^{-1})=100+\alpha E_j$;

Model EB (exponentially weighted Boltzmann): $p_{ij}=c_4 N(E_i) \exp(-E_i/RT) \exp(-\Delta E/\langle\Delta E\rangle)$;

Model GB (gaussian weighted Boltzmann): $p_{ij}=c_5 N(E_i) \exp(-E_i/RT) \exp\{-(\Delta E-\Delta E_{mp})^2/2\sigma^2\}$;

the c's are normalization constants; $\langle\Delta E\rangle$, ΔE_{mp} (mp signifies most probable), β and σ are parameters of the models; $\langle\Delta E\rangle$, or ΔE_{mp}, were constant in all cases except for Model LG; σ was set equal to 0.7 ΔE_{mp}; $N(E_i)$ is the density of states for a cyclobutene molecule of internal energy E_i. An early computational feature (desirable to limit the probability matrix $\underset{\sim}{P}$ to tractable dimensions) imposed a limit of 9000 cm^{-1} on ΔE $(=E_j-E_i)$; then $p_{ij} = 0$ for $\Delta E > 9000$ cm^{-1}.

Detailed balance and completeness were maintained. Due to the limitacion in the size of $\underset{\sim}{P}$, the values of $\langle\Delta E\rangle$ and ΔE_{mp} are related to, but not necessarily equal to, the effective average down transition size $\langle\Delta E'\rangle$; (note: $\langle\Delta E'\rangle$ some models varies with the initial energy of the cyclobutene molecule, and in these cases the value of $\langle\Delta E'\rangle$ at the critical reaction threshold energy (E_0) has been used to characterize the size of the down step). Later calculations were made with a limit on ΔE of 18,000 cm^{-1}; the value of $\langle\Delta E'\rangle$ is found to be substantially invariant.

Models EB and GB have functional forms which, in the limit of very large average amounts of energy transferred per collision, approach strong collider behavior more closely than do models FE, FG and LG. True strong collider behavior will not be precisely observed owing to the limitation on the size of $\underset{\sim}{P}$.

The microscopic rate constants for the isomerization of cyclobutene molecules were calculated from RRKM theory using the frequency assignments of "Model C" of Elliott and Frey [6], but with removal of the accidental commensurability employed by them. Variation of k_E with E is shown in Fig 2 along with corresponding plots for cyclopropane and cyclobutane. The fraction of molecules excited to energy levels above E_0 which undergo reaction is > 98% for cyclobutene, compared to $\sim$ 75% and 20% for cyclopropane and cyclobutane, respectively. Thus, cyclobutene is virtually in the second order region where the critical energy threshold constitutes an ideal absorbing barrier.

The results of the computer simulation calculations are included in Fig 1, and the model parameters that fit the experimental data are listed in Table II. As in previous work [1], a value of $\langle\Delta E'\rangle$ was found at each temperature by fitting the calculations to the experimental data for the m = 2.6 reactor. It should be noted that the calculated curves in Fig 1 have been shifted by 14 K to lower temperatures and by 0.10 log units to higher values of log $\bar{P}_c(m)$. These

shifts bring the calculated value of $\bar{P}_c(m)$ for a strong collider and the experimental value of $\bar{P}_c(m)$ at the lowest temperature in the m = 27.2 reactor into agreement. The required shifts are not large and reflect the combined experimental and theoretical uncertainties. For example, a decrease in the true value of the activation energy of the reaction by 300 cm^{-1} (an amount easily within the experimental uncertainty), with concomitant reduction of the pre-exponential factor from 2.5×10^{13} s^{-1} to 1.3×10^{13} s^{-1}, is equivalent to shifting the calculated curves to lower temperatures by $\sim$ 10 K. Also, anharmonicity effects, whilst unimportant (partially self compensating) when estimating unimolecular rate constants near the high pressure limit, are much more important at the low pressure limit. Anharmonicity effects increase the fraction of molecules that reach the critical energy for reaction. In the present instance, we consider that an increase in the low pressure rate of 20-25% due to anharmonicity effects is quite reasonable (for example, the rate constant for isomerization of methyl isocyanide was estimated to increase by 25 - 40% when anharmonicity effects were taken into account [8]); this is equivalent to a shift of the calculated values by 0.10 log units along the log $\bar{P}_c(m)$ axis.

Included for comparison in Fig 1 is the calculated curve for strong collider behavior. This curve is essentially the same for all values of m (it would be identically the same if the free-flight times (between wall collisions) were the same for all reactors, or if the system was in the second order region rather than in the fall off region. Model FE is the most difficult to fit to data that approach strong collider behavior at the lowest temperature.

Discussion

The experimental results shown in Fig. 1 are qualitatively in total accord with previous work [1-5]. As before, the data for the reactor with m = 27.2 may be considered as effectively representing steady-state limiting behavior. The data for the reactor with smallest mean collision numbers, m = 2.6, deviate most from strong collider and from steady state behavior, while the deviation decreases with decreasing temperature. This indicates that the surface behaves as a progressively stronger collider as the temperature is decreased. Thus, the present results at the lowest temperatures extend the trend noted in the earlier studies conducted at higher temperatures: the values of $\bar{P}_c(m)$ become virtually independent of the mean collision number, and the curves of $\bar{P}_c(m)$ vs temperature become coincident at temperatures below $\sim$ 400 K - 450 K. This behavior graphically demonstrates that at the lowest temperatures the surface is behaving as an ideal strong collider: each collision with the surface effectively brings the molecule into thermal equilibrium with the wall. This significant conclusion is independent of calculational models, parameters or detailed deconvolution of the data.

Incubation times [1] are 4.4 at 778 K for both Models FE and FG, and decrease to 3.5 and 3.1 at 585 K for FE and FG, respectively.

In previous work with cyclopropanes [1,3,4] stochastic modeling of the energy transfer processes resulted in Model FG, as well as a linear exponential model, LE (i.e., Model FE but with $\langle\Delta E\rangle$ = constant + αE_j), providing the best fit; however, for cyclobutane [2], and methylcyclopropane [5], where wall collisions were found to be weaker than in the cyclopropane system, Model FE provided the best fit, although the fits of Model FG and Model LE were also reasonable. From the curves in Fig 1, it can be seen that both Models FE and FG give quite good fit to the cyclobutene data in the higher temperature region that overlaps the lower temperature portion of the cyclobutane study. The

values of $\langle \Delta E' \rangle$ resulting from the calculations vary from 2150 cm^{-1} for both models, at 778 K, to 5150 cm^{-1} and 3600 cm^{-1} for Models FE and FG, respectively, at 585 K (Table II). For comparison, the value for cyclobutane [2] at 778 K was $\sim$ 2290 cm^{-1} (Model FE). At comparable temperatures, therefore, the difference between cyclobutane and cyclobutene is not great, even though the critical energy for the former reaction (20,700 cm^{-1}) is approximately twice that of the latter (11,300 cm^{-1}). It could be tempting, therefore, to conclude that the correct model for energy transfer probably is one in which the average amount of energy transferred did not vary greatly with the energy content of either of these highly energized species. However, in the present study (Table II), it can be seen that <u>all</u> the models of energy transfer used give an adequate fit to the cyclobutene data, while Models LG, EB and GB are such that $\langle \Delta E' \rangle$ <u>does</u> vary with molecular energy content. We have applied Models LG, EB and GB to the cyclobutane data [2], and they are found to give worse fit than the Models FE and FG.

It is evident that for a clearer distinction to be made between the various models for energy transfer, it would be desirable, but difficult, to obtain data at much higher temperatures than have been investigated. For the case of efficient collisions, data obtained at low temperatures do not provide adequate distinctions, although they do suffice here to illustrate the failure of a simple exponential model (FE), a conclusion that now has long standing [9] from steady state work.

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Table I

Mean probabilities for reaction of cyclobutene per collision with the reactor wall, $\overline{P}_c$ (m).

Reactor (i)	Temp.(K)	643	577	512	461	429	
m = 27.2	$\overline{P}_c(m)\times10^7$	477	46.8	2.06	0.0995	0.0112	
Reactor (ii)	Temp.(K)	665	585	516	463		
m = 8.5	$\overline{P}_c(m)\times10^7$	736	53.7	2.28	0.112		
Reactor (iii)	Temp. (K)	778	731	668	585	523	469
m = 2.6	$\overline{P}_c(m)\times10^7$	1930	844	230	21.0	1.91	0.122

Table II. Calculated mean probabilities for reaction of cyclobutene molecules per collision with the reactor wall, $\bar{P}_c(m)$ for various energy transfer models.

Temp(K)	Model	$\langle\Delta E\rangle, \Delta E_{mp}$ (cm^{-1}) or α	$\langle\Delta E'\rangle$ (cm^{-1}) at E_o	$-\log \bar{P}_c(m)$ SC[a]	m=27.2 calc	m=27.2 expt	8.5 calc	8.5 expt	2.6[b]
	FE	6400	5150		5.47		5.54		
	FG	3300	3600		5.44		5.50		
571	LG	0.40	4500	5.30	5.44	5.44	5.51	5.53	5.90
	EB	1100	5850		5.40		5.48		
	GB	1750	3700		5.39		5.45		
	FE	3200	3040		4.29		4.37		
	FG	2350	2600		4.24		4.32		
652	LG	0.32	3950	4.00	4.20	4.20	4.30	4.30	4.81
	EB	1120	4500		4.17		4.27		
	GB	1600	2950		--		4.26		
	FE	2400	2150	2.75	3.20		3.29		3.78
764	FG	1960	2150		3.12		3.21		

a) Limiting strong collider value

b) The calculated value for each model was adjusted to fit experiment for m = 2.6; see text.

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[2] M. C. Flowers, F. C. Wolters, B. D. Barton and B. S. Rabinovitch, Chem. Phys. 47 (1980) 189. Note the following erratum in this reference: the right ordinate of Fig 5 should carry the legend, $P(n)x10^4$.

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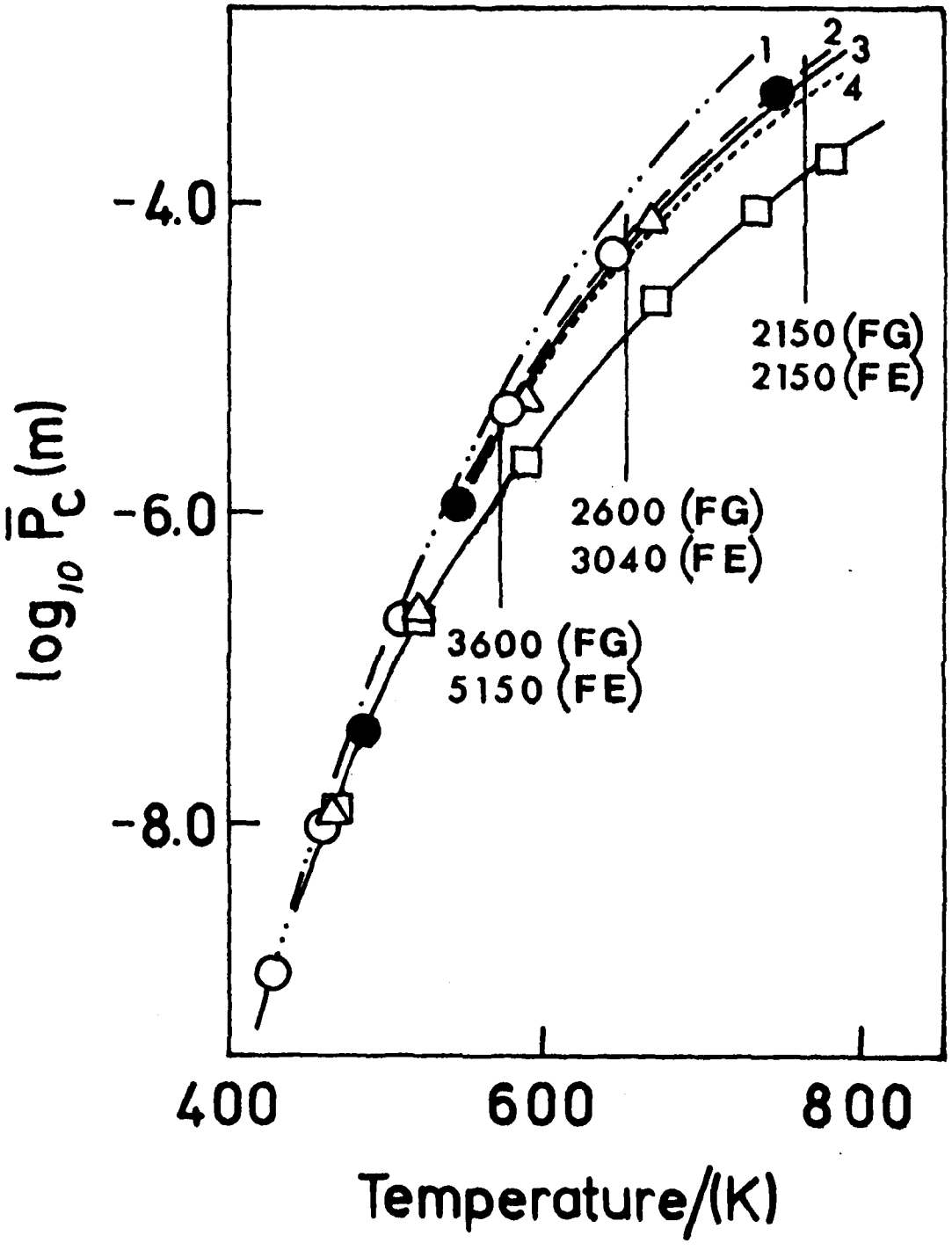
Figure legends

Fig. 1 Plot of calculated and experimental values of $\log_{10} \tilde{P}_c(m)$ vs temperature for cyclobutene. Experimental data: ○, m = 27.2; △, m = 8.5; ●, m = 5.9; □, m = 2.6. Calculated data: curve 1, strong collider; curve 2, Model FG, m = 27.2; curve 3, Model FE, m = 27.2 and Model FG, m = 8.5, which coincide; curve 4, Model FE, m = 8.5. All models were fitted to the m = 2.6 data. Values of $\langle \Delta E' \rangle$ (the model used is indicated in parenthesis) used to fit the curves to the experimental data are indicated at three temperatures.

Fig. 2 Calculated plots of the microscopic reaction rate constants, k_E, vs energy (cm^{-1}) for cyclobutene (E_0 = 11,400), ○; cyclopropane (E_0 = 22,300), ▽; and cyclobutane (E_0 = 20,800), □.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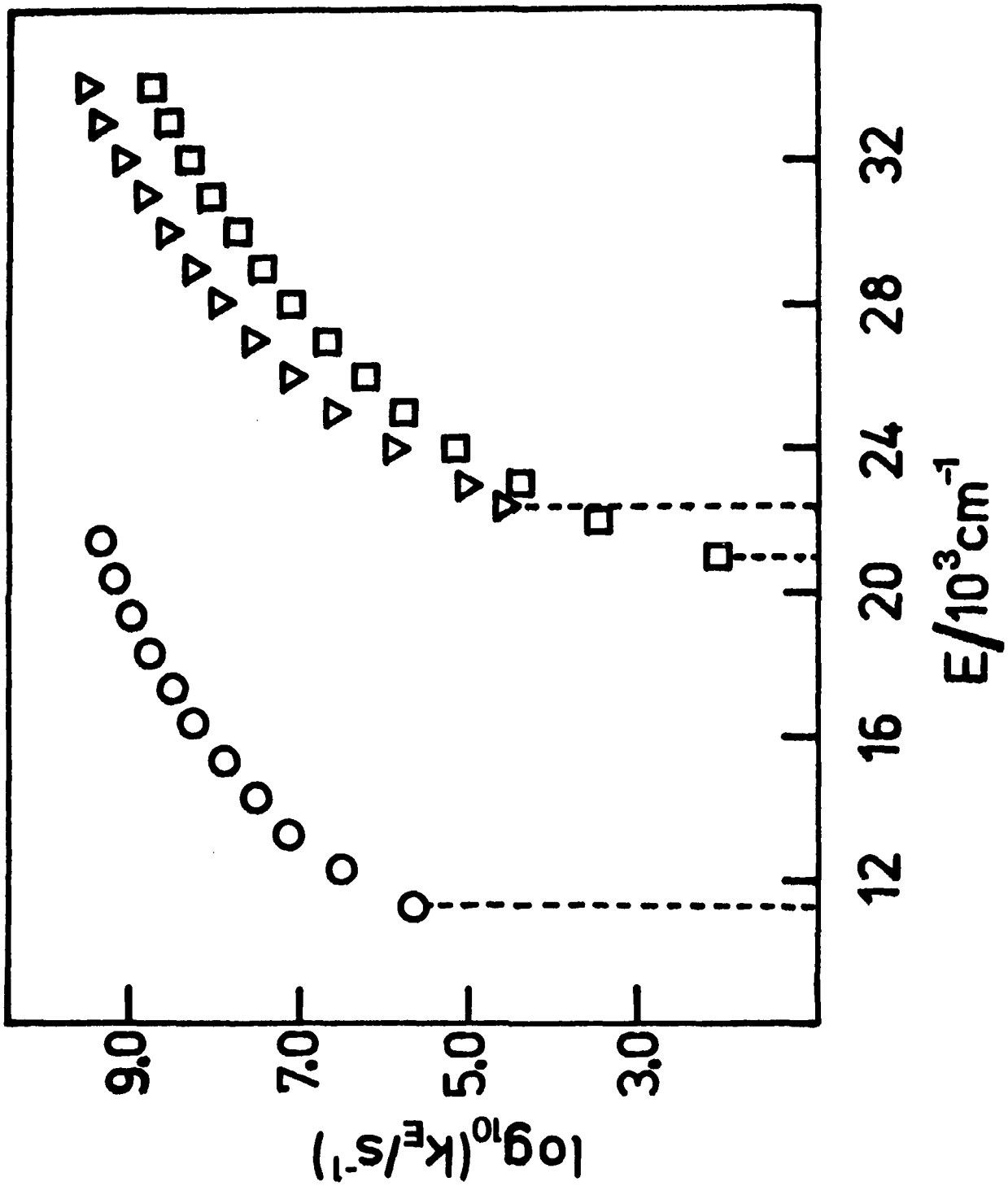

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